Supplementary Information

A “Counter-charge Layer in Generalized Solvents” Framework for Electrical Double Layers in Neat and Hybrid Ionic Liquid Electrolytes

Guang Feng[†,*], Jingsong Huang[‡], Bobby G. Sumpter[‡], Vincent Meunier[§], and Rui Qiao[†,††]

[†] *Department of Mechanical Engineering, Clemson University, Clemson, South Carolina 29634-0921*

[‡] *Oak Ridge National Laboratory, Bethel Valley Road, Oak Ridge, Tennessee 37831-6367*

[§] *Department of Physics, Applied Physics, and Astronomy, Rensselaer Polytechnic Institute, Troy, New*

1. Oscillatory orientation of ACN dipole near electrode surface

Figure S1 shows the concentration and dipole orientation profiles of the ACN molecules near a positive electrode ($\sigma = 0.1$ C/m^2) in contact with hybrid electrolyte with 50% ACN and 50% [BMIM][BF$_4$]. As expected, the dipole of the first ACN layer adjacent to the electrode is oriented mainly away from the electrode surface. However, the ACN molecules adjacent to the

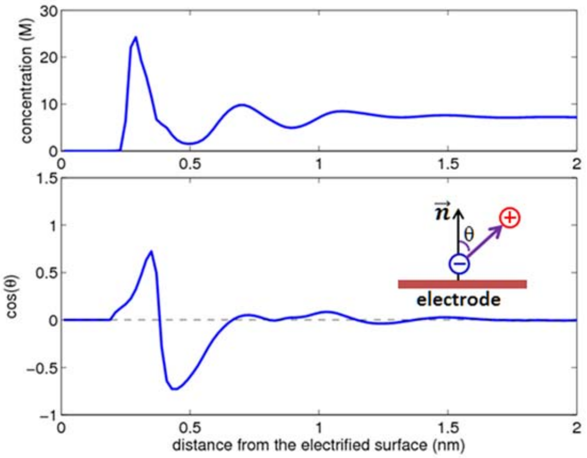

Figure S1. Concentration (panel **a**) and average dipole orientation $\langle\cos\theta\rangle$ (panel **b**) profiles of ACN molecules near electrodes with surface charge density of 0.1 C/m^2. The electrolyte is made of 50% ACN (mass fraction) and 50% [BMIM][BF$_4$]. θ is defined as the angle spanned by the dipole of an ACN molecule (pointing from the negative charge to the positive charge) and the normal direction of the electrode surface. The position of ACN molecules is based on their center of mass.

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[*] Present address: Department of Chemical & Biomolecular Engineering, Vanderbilt University.

[††] Corresponding author. Email: rqiao@clemson.edu, URL: http://www.clemson.edu/~rqiao

first ACN layer orient their dipole toward the electrode, and the oscillatory distribution of ACN dipole penetrates about 1.5 nm into the bulk electrolyte. The alternating orientation of the dipole of ACN molecules observed here is very similar to that described for the generalized solvents in the main text.

2. Derivation of Equation (4)

The derivation is similar to that reported in one of our prior paper,[1] and is detailed here for completeness. We consider an EDL near an open planar electrode with a surface charge density of σ (see Figure S2). The potential distribution inside the EDL observes the Poisson equation

$$\frac{d^2\phi}{dy^2} = -\frac{\rho_e(y)}{\varepsilon_0} \tag{S1}$$

Set the potential ϕ in the bulk electrolyte to zero and integrate Equation (1) twice, we have

$$\phi(y) = -\frac{1}{\varepsilon_0}\int_0^y \int_0^{y'} \rho_e(x)\, dx\, dy' \tag{S2}$$

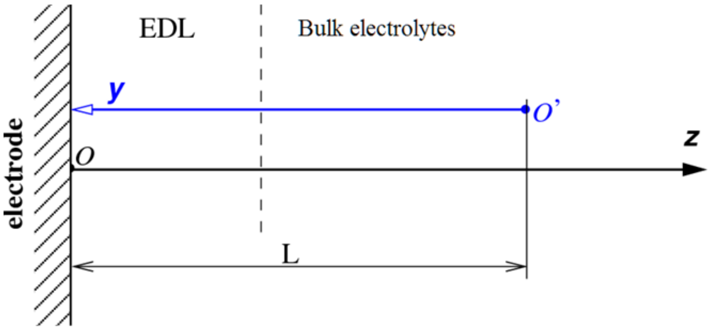

Figure S2. Schematic of an EDL near a planar electrode in equilibrium with bulk electrolytes. Two coordinate systems are used to derive the potential drop across the EDL. The first, y-coordinate system has its origin in the bulk electrolyte liquids, where the space charge density is zero. The second, z-coordinate system has its origin at the electrode surface.

Using integration by parts, Equation (2) is transformed to

$$\phi(y) = -\frac{1}{\varepsilon_0}\int_0^y (y - y')\, \rho_e(y')\, dy' \tag{S3}$$

Therefore, the potential drop across the EDL is

$$\Delta\phi_{\mathrm{EDL}} = \phi(L) - \phi(0) = -\frac{1}{\varepsilon_0}\int_0^L (L-y')\,\rho_{\mathrm{e}}(y')\,\mathrm{d}y' \tag{S4}$$

Since $L - y$ is the distance between point y and the electrode surface (see Figure S2), Equation S4 can be transformed to the z-coordinate system as

$$\Delta\phi_{EDL} = -\frac{1}{\epsilon_0}\int_0^L z\rho_e dz \tag{S5}$$

In the absence of molecular solvents, using Equation (S5) and the space charge as given in the lower portion of panel **a** in Figure 5 (reproduced here as Figure S3), we obtain

$$\Delta\phi_{RTIL\_only} = \sigma\left[d_0 + \textstyle\sum_{i=1}^{N}(-1)^i\gamma_i\Delta_i\right]/\varepsilon_0 \tag{S6}$$

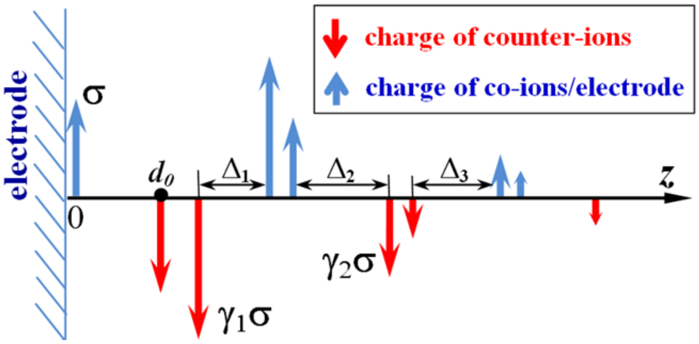

Figure S3. Distribution of space charge inside EDLs described by the "counter-charge layer in generalized solvents" framework. Here only RTILs are present inside the EDL. See main text for the definition of symbols.

Using Equation (4), it is straightforward to show that the contribution of the molecular solvents to the potential drop across EDL is

$$\Delta\phi_{solvents} = \sigma[-N_{sol}\mu_{sol}\langle\cos\theta\rangle]/\varepsilon_0 \tag{S7}$$

where N_{sol} is the amount of solvent molecules inside the entire EDL per unit area scaled by the electrode surface charge density, μ_{sol} is the dipole moment of each solvent molecule, and $\langle\cos\theta\rangle$ is the average dipole orientation of all solvent molecules inside the EDL with respect to the normal direction of the electrode surface. Combining Equations S6 and S7 will lead to Equation (4) in the main text.

Reference

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[1] G. Feng, J.S. Zhang and R. Qiao, *J. Phys. Chem. C* **113**, *4549*, 2009.